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DEVELOPMENT OF AIR SAMPLING METHODOLOGY

Bernard E. Saltzman

Cincinnati University

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May 1975

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DEVELOPMENT OF AIR SAMPLING METHODOLOGY

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Solid absorbent systems were developed for analysis of three gaseous ambient air pollutants. Nitrogen dioxide was sampled with small glass tubes packed with copper shot, which could be used as personal samplers, and be stored before analysis for up to 5 weeks. Reactive hydrocarbons were determined in a dual analyser as the concentration absorbed on chromium trioxide-sulfuric acid. These monitoring measurements should correlate better with photochemical reactivity than those of non-methane hydrocarbons. Permeation tubes for vinyl chloride were critically examined and successfully used to optimize the carbon tube sampling method. Time patterns of monitoring data were examined by Fourier analysis on a computer.

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CHEMICAL METHODS	REACTIVE HYDROCARBON	17-AIR QUAL. MEAS
MEASUREMENT METHODS	VINYL CHLORIDE	
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ABSTRACT

Major efforts were focussed on use of solid absorbents to provide simple, compact, and inexpensive, yet reliable gas sampling and analysis systems for three gaseous pollutants: nitrogen dioxide, "reactive" hydrocarbons, and vinyl chloride. Time fluctuations of monitoring data by computer analyses showed alignment of Fourier spectra for common pollutants.

Nitrogen dioxide was sampled with small glass tubes packed with copper shot. This device could be readily used as a personal dosimeter, as well as at a fixed station. The tubes were capped, and could be stored for up to 5 weeks. Nitrogen compounds released by heating the tube in a stream of hydrogen were passed into a catalytic furnace, converted to ammonia, and reproducibly determined with a conductivity detector.

The dual system for monitoring hydrocarbons with an FID detector passed one sample stream through a chromium trioxide-sulfuric acid absorbent and the other through a bypass. Conditions were adjusted to obtain complete response (taken as the difference) to olefins and partial response to aromatics, to parallel photochemical reactivity.

Permeation tubes containing vinyl chloride were evaluated as standards for calibrating gas chromatographs in analysis of air for this gas. Permeation rates and their temperature coefficients were determined for FEP and TFE Teflon for up to 8 months. Best conditions for sampling with charcoal tubes,

desorption with carbon disulfide, and analysis by injection into a gas chromatograph were determined.

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SECTION 1

CONCLUSIONS

A small glass tube packed with copper shot provided a simple, compact, convenient, and effective means for sampling ambient air for low concentrations of nitrogen dioxide, for periods varying from a few minutes to 24 hours. Interfering high concentrations of sulfur dioxide were removed by a filter impregnated with potassium carbonate. The exposed tubes were sealed with Teflon plugs, and could be stored for 35 days with only 11% loss. The analytical system which included heating in a stream of hydrogen, converting released nitrogen compounds to ammonia in a furnace train, and determining them with a Coulson Conductivity Detector, yielded a reproducible stoichiometric factor of 59%. This sampling tube is small enough for use as a personal sampling device, and could be reused repeatedly after each analysis.

A monitoring system for total and "reactive" hydrocarbons was developed by adapting a current commercial total hydrocarbon analyzer, and was successfully used in Cincinnati. Response was based on the difference between cyclical measurements on sample air, and on the air passed through an absorbent. It could be adjusted to parallel photochemical reactivities of various classes of hydrocarbons. This should provide more significant measurements than those currently made of non-methane hydrocarbons, and makes feasible an improved air quality standard.

Sampling and analysis of ambient concentrations of vinyl chloride were critically examined. Teflon permeation tubes were found to be accurate means of providing known low concentrations for testing carbon tube sampling methods and calibrating gas chromatographs. Analytical methodology was optimized to provide 90% recovery even after two weeks of sample storage.

Computer analysis of air monitoring data for Cincinnati yielded Fourier spectra for lead, sulfur dioxide, and hydrocarbons. Similar patterns were obtained for fluctuations of corresponding time periods. Further work should clarify atmospheric processes, the relationships between pollutants, and should produce improved models of concentrations.

SECTION II

RECOMMENDATIONS

It was not possible within the funding made available to fully develop and field test the methods described. The scope was limited to exploration, determination of feasibility, and critical examination of significant parameters. Efforts were focussed on three important pollutants. We believe that the results justify continued work for ultimate routine application of these procedures.

SECTION III

INTRODUCTION

Recent legislation has resulted in a great expansion of work in air quality monitoring by multiple networks. This has accentuated the constant need for simplified, more convenient, and more accurate analytical methods. Rapid advances in analytical instrumentation and detectors can be applied to air pollution with appropriate testing and development. The low concentrations of pollutants specified in the Air Quality Standards require measurements at the limits of sensitivity and specificity of many available procedures and instruments. Greater accuracy is needed not only because of legal and economic significance of the measurements, but also for scientific studies of health and economic effects. The dosimetric personal sampling approach to study of health effects requires reduction in size and weight of sampling devices.

A broad scope of investigations was originally proposed for this project. However, limitations of funding that was made available reduced the work to exploration and initial development of devices for three gaseous pollutants: nitrogen dioxide, reactive hydrocarbons, and vinyl chloride. Computer analysis of air monitoring data to extract information on temporal patterns of fluctuations also was explored. The work has been fully described and references in manuscripts prepared for appropriate scientific journals. These are submitted in the

Appendices. In order not to preclude their acceptance and publication, we request that they not be published with this final report. Major aspects of each paper are given in the text which follows.

SECTION IV

SOLID ABSORBENT METHOD FOR SAMPLING AND ANALYSIS OF NITROGEN DIOXIDE IN AMBIENT AIR

A small sampling device was designed to obtain time integrated exposures to nitrogen dioxide in ambient air. One basic objective of the research effort was to meet the need for generating data on personal exposures as contrasted with the presently available data obtained from continuous monitoring instruments at fixed locations. The ideal requirements for a personal dosimeter sampling device were set up as follows: (1) small convenient size which can be carried during daily routine; (2) economical to make and analyze; (3) accurate; (4) stable before and after sampling; and (5) free of common interferences.

A solid absorbent system was selected as best meeting the requirements. Some of the more commonly used absorbents were examined as well as active metals and metal oxides. Copper metal was chosen for extensive studies since it was compatible with a number of possible analytical systems. Studies were focused on the ability of the copper to absorb a reproducible fraction of the incoming ambient nitrogen dioxide under a variety of sampling conditions and ambient air conditions. The final sampling tube design is shown in Figure 1. It is small enough to be worn with a small sample pump without encumbering the wearer.

Sample tubes were constructed of borosilicate glass and

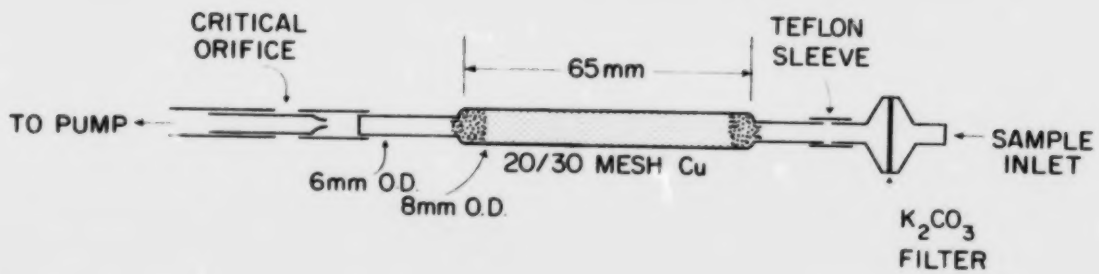

Figure 1 Sampling train for NO_2

packed with copper shot. The copper was purified and activated by heating under a stream of hydrogen. The cooled absorption tube could be stored for weeks before use. For use the tube was opened and connected to a small pump. A filter impregnated with potassium carbonate was placed on the inlet of the adsorption tube, to remove sulfur dioxide which was a negative interference. A sample was then drawn through the adsorption tube for a period of time up to 24 hours. When small personal pumps are used the critical orifice shown may be omitted, and the flow adjusted with the pump mechanism. Upon completion of sampling the tube was sealed and could be analyzed at the laboratory within 5 weeks.

Analysis was performed by catalytic reduction of the nitrogen containing compounds absorbed on the copper. A small furnace as shown in Figure 2 was used to drive the absorbed nitrogen compounds into the catalytic furnace where all nitrogen compounds were converted to ammonia. Any acidic compounds which could interfere were removed by the potassium carbonate section of the furnace. The ammonia was then analyzed by a Coulson Conductivity Detector. Calibration of peak areas was accomplished by introducing a known volume of standard silver nitrate solution into empty absorption tubes and following the same heating procedure. This standard was convenient and the nitrogen content was completely converted to ammonia.

Parameters of the sampling and analysis system were studied to ensure specificity and to determine recoveries. A total of 84 sample runs were made. A reproducible stoichiometric factor of 58.8% was found. Consistent linear responses were found under a variety of sampling conditions as shown in Figure 3. Storage effects also were studied and it was found

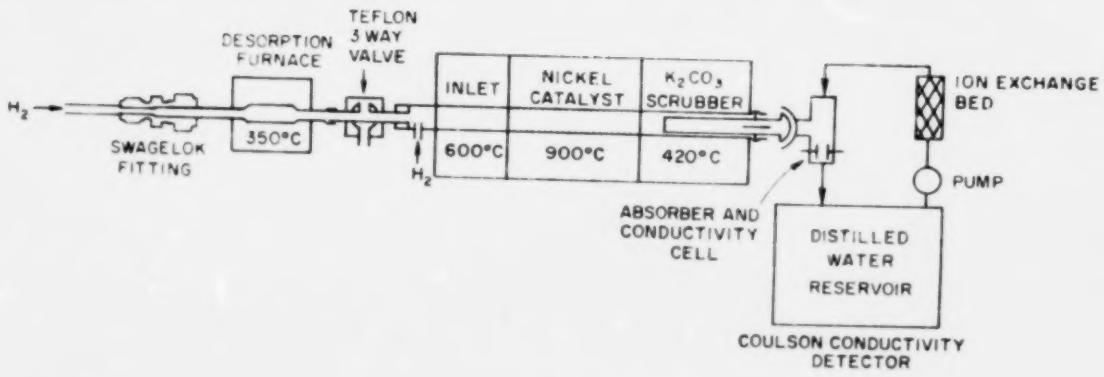

Figure 2. Desorption and detection system.

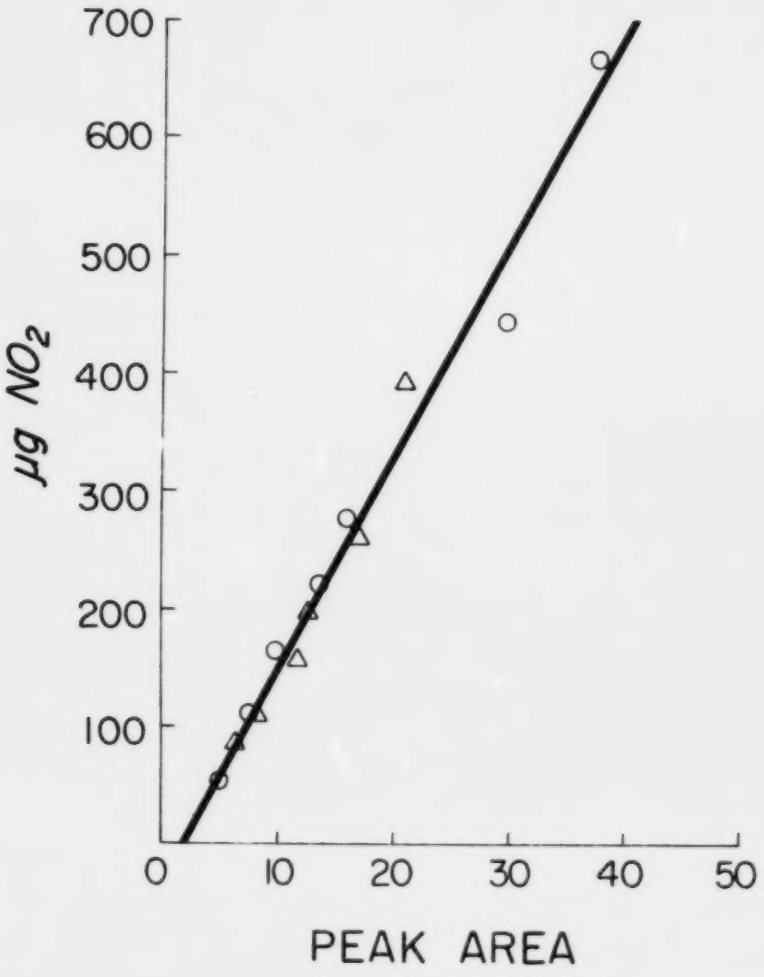

Figure 3. Performance of method for different sampling conditions.

0 - Varying times of sampling 0.164 ppm NO_2 at constant flow rate.

Δ - Varying concentrations of NO_2 sampled for a constant time at constant flow rate.

that the tubes could be stored after sampling for up to 35 days and still have an acceptable, although decreased, precision. Analyses of ambient air samples collected for a twenty-four period were compared with the data from the Cincinnati air monitoring station and showed a 0.776 correlation coefficient.

In conclusion the copper absorbent method has shown promise as a possible personal monitoring device suitable for time-integrated sample collection. The device is relatively inexpensive and can be reused. The samples may be shipped to a central laboratory for analysis by skilled technicians. The procedural techniques developed may be applied to a number of other pollutants such as SO_2, H_2S or HCl with the proper selections of absorbents and sample analysis trains.

This work is completely referenced and supporting data are included in the Appendix.

SECTION V

CONTINUOUS MONITORING INSTRUMENT FOR "REACTIVE" HYDROCARBONS IN AMBIENT AIR

The objective of this effort was the development of a monitoring instrument with specific responses to the classes of hydrocarbons with the greatest potential for forming photochemical smog. Common instruments are used to monitor total hydrocarbons or total hydrocarbons minus methane. Either of these measurements is only partially successful as a predictor of the severity of the smog that later develops.

Two two main stages of this study were the selection and characterization of a solid chemical absorbent capable of removing the olefinic and aromatic hydrocarbons primarily responsible for smog, and the construction and testing of a dual monitoring instrument incorporating this absorbent which determined both total and reactive hydrocarbons.

The instrument, shown schematically in Figure 4, was assembled from commercially available components: a Beckman Model 109A Hydrocarbon Analyzer, a thermostated valve oven (Carle Model 4301) containing the absorbent, an 8-port microvalve (Carle Model 2012) turned by a valve actuator (Carle Model 4201) operated by a timer (Carle Model 4102). Two equal flows of sample air were passed through the absorbing column and an empty column. The output from each column was alternately directed by the valve to the flame ionization detector or vented in a timed five-minute cycle.

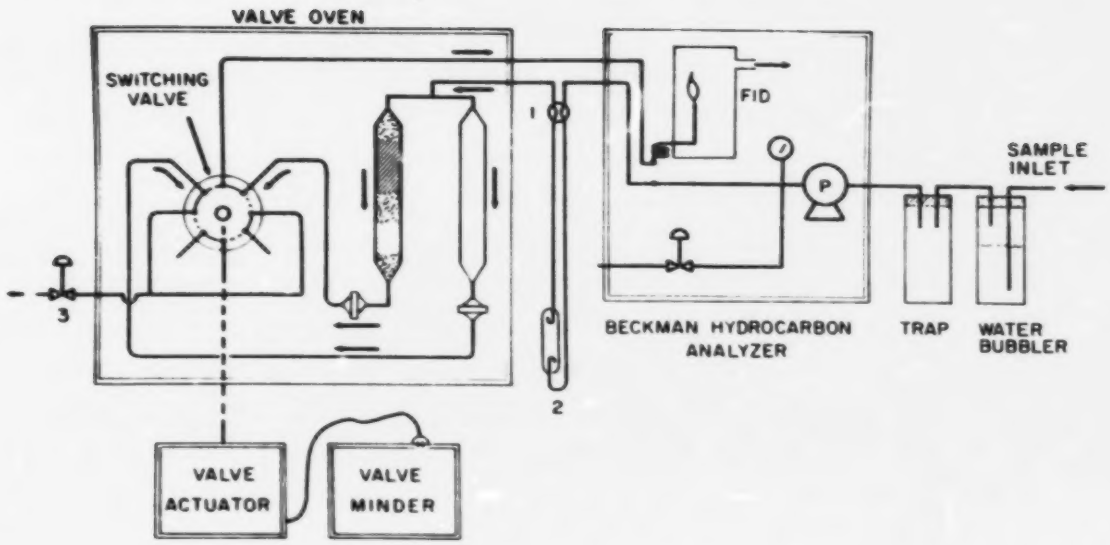

Figure 4. Schematic of the hydrocarbon monitoring system.

Candidate absorbents were screened for their ability to remove olefins from a sample stream without affecting paraffins. A chromium trioxide-sulfuric acid mixture on 60-80 mesh chromosorb possessed the most desirable absorbent characteristics and was selected for more detailed study. The effects of moisture, flow rates and temperature on the ability of the absorbent to remove various hydrocarbons were examined. Figure 5 summarizes some exploratory studies with propane and propene and shows the effects of temperature and contact time. It was found that to obtain reliable results it was necessary to humidify the air sample stream by passing it through an upstream bubbler containing water. Under constant humidity conditions, the responses for important hydrocarbons were determined. The absorber characteristics can be adjusted by changing the absorbent column temperature or dimensions. The optimal temperature for the absorber was 74°C, at which the response characteristics best matched the photochemical reactivities of various types of hydrocarbons.

Ambient air was monitored for hydrocarbons for more than a month from a second-story window in the laboratory. Figure 6 shows a typical recording giving the usual pattern for total and reactive hydrocarbon concentrations for elevated morning and evening levels. Short-term studies indicated the method was practical, reliable and accurate and can provide new information about air quality.

Complete details are given in the Appendix.

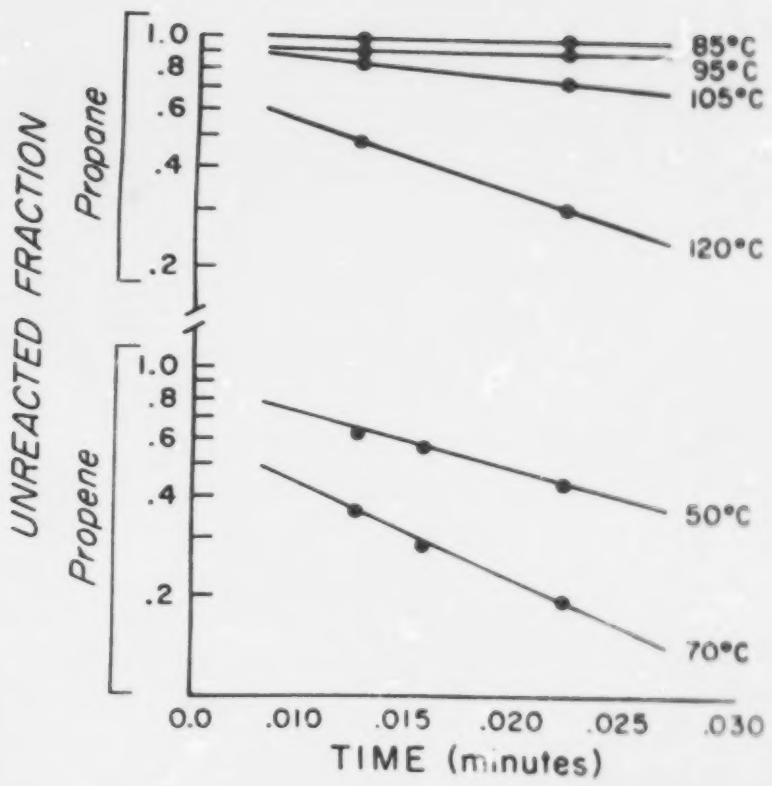

Figure 5. Preliminary studies of effects of temperature and contact time on the absorbent performance.

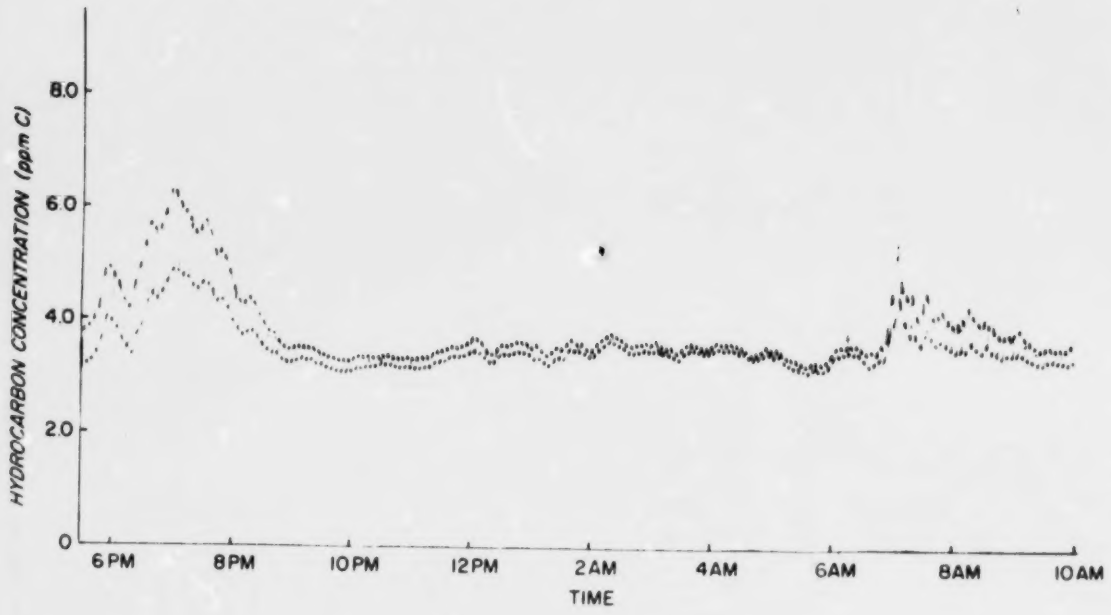

Figure 6. Recording from instrument of ambient air in Cincinnati on June 2, 1973. Upper half of each 5-minute cycle shows total hydrocarbon concentration, and the decrease to the lower half is the reactive hydrocarbon concentration.

SECTION VI

CALIBRATION OF A GAS SAMPLING VALVE

FOR GAS CHROMATOGRAPHY

The multiport gas sampling valve with a sample loop of known volume is in widespread use for chromatographic analysis of gas mixtures. The volume of sample which is actually passed into the gas chromatograph usually differs from the loop volume stated by the manufacturer, because it also includes the volume of all of the connecting tubing and dead space in the valve. These vary with custom mounting or design differences. In many analytical situations the true sample volume need not be known exactly, since comparisons are made between identical volumes of standards and samples in the calibration procedure. However, sometimes, it is necessary to know the sample volume. In the present case, it was desired to compare samples of vinyl chloride in air with standards of vinyl chloride in a solvent introduced by syringe injections onto the same column. The exact volume of the loop was therefore determined by a novel application of the method of standard additions.

The stainless steel loop labelled 2cc was removed from the instrument, and filled with water from a 10 ml buret. The tube was dried and the operation repeated twice. The average volume was determined as 2.43 ml. Three more loops were made from 1/8-in. copper tubing, and their volumes determined in the same manner as 0.66, 0.32 and 0.22 ml. Then a fixed

gaseous concentration of vinyl chloride was sampled successively with each of the loops in place in the gas chromatograph, and the corresponding peak heights were determined. The gas mixture was provided by a permeation tube and flow dilution system although a plastic bag also could have been used. It was not necessary to know its exact concentration, but only that it was constant and within the linear dynamic range of the detector.

A plot was made of the peak heights as ordinate vs. the measured sample loop volumes as abscissas. A straight line fitted by the method of least squares was extrapolated to the X axis, which it intersected at -1.38 ml. Thus the permanent volume was determined to be 1.38 ml, and the actual volume of sample 3.81 ml rather than the nominal 2 cc. This method was convenient, did not require shutting down the instrument or removal of plumbing other than the loop, and required only a buret or balance for the calibration. Complete details are given in the Appendix.

SECTION VII

USE OF PERMEATION TUBES FOR CALIBRATION OF VINYL CHLORIDE ANALYSES

Recent recognition of the carcinogenic hazards associated with vinyl chloride exposure generated the need to monitor ppm levels in work areas and ambient air. Accurate analysis is essential. The Environmental Protection Agency recently published a tentative method of analysis for ambient air concentrations similar to that recommended by the National Institute for Occupational Safety and Health for occupational areas. Both methods were based on adsorption of vinyl chloride on charcoal, desorption into carbon disulfide and injection into a gas chromatograph for determination with a flame ionization detector. Quantitative results were obtained by comparing the sample responses to those from known concentrations. The accuracy of the method was thus dependent upon the accuracy of the standards as well as of the sampling procedures. Standards were prepared by gravimetric and volumetric procedures. Gravimetric techniques were used to determine the weight of vinyl chloride absorbed when it was bubbled through toluene; aliquots of this solution were diluted with carbon disulfide. Standards were also prepared volumetrically using measured volumes of the vinyl chloride gas which were injected directly into carbon disulfide. Both of these methods were somewhat inconvenient and subject to errors from volatilization.

Permeation tubes have proven useful in preparing continuous, low level concentrations of a variety of gaseous compounds. Their performance with each individual compound, however, must be determined experimentally since a stable permeation rate cannot be achieved if the tubing is affected by the permeant gas or if the liquified contents polymerize, decompose or react with the dilution air. The purpose of this work was to prepare and evaluate permeation tubes for generating accurate gaseous vinyl chloride standards.

Permeation tubes were made from 0.250" O.D. x 0.030" wall thickness tubing of both FEP (fluorinated ethylene propylene copolymer) and TFE (tetrafluoroethylene polymer) Teflon. A long-lived tube also was constructed using an 8 ml stainless steel bottle. After the tubes were filled with liquid vinyl chloride the ends were plugged with a Teflon rod secured with Swagelok ferrules.

Permeation rates were determined gravimetrically over periods up to 8 months, during which the tubes were held at three temperatures in a cyclical pattern. Several weighings were made at each temperature and the slopes of plots of weights versus age were used to determine the rates. Results are shown in Figure 7, which is an Arrhenius-type plot in which the abscissa scale is proportional to the reciprocal of absolute temperature, and the ordinate is a logarithmic scale of permeation rates. Lines were fitted to the data by the method of least squares. The rates at 25°C for FEP and TFE Teflon were respectively 0.259 and 1.98 ug/cm min., and from the slopes the activation energies of permeation were calculated to be 15.0 and 11.9 kcal/g mol.

The monomeric liquid vinyl chloride remained stable in the permeation tubes which were exposed to flows of dry dilution air for periods as long as eight months. A stable permeation

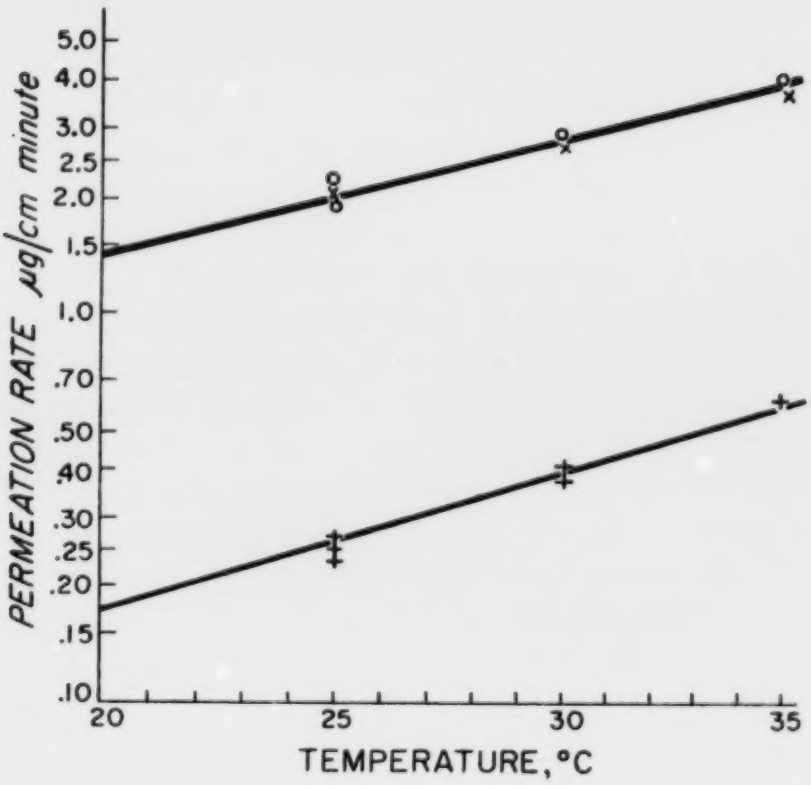

Figure 7. Permeation rates of vinyl chloride in Teflon tubes of 0.250" o.d. x 0.03" wall thickness.

+ FEP Teflon, 14 cm long

x TFE Teflon, 20 cm long

0 TFE Teflon, 11 cm long, with 8 ml. stainless steel bottle

rate was maintained when the tube was kept at a constant temperature. For greatest accuracy, it was found desirable after a temperature cycle to determine the new permeation rate. The relative standard deviation of the permeation rate for a 2-month period was 1.1 percent.

These gaseous standards can give very precise calibrations when the gas sampling valve is also used for gaseous samples for injection into the column in an identical manner. Alternatively, the gaseous standards can be used with the charcoal tube sampling procedure in which a liquid sample is injected into the instrument.

The vinyl chloride permeation tube was found to be a convenient and accurate device for making low level mixtures of vinyl chloride in air. Application of the permeation tube system is not limited to generation of standard samples; the device can also be used for animal exposure studies since the tube lifetimes are on the order of two-thirds of a year. The permeation device is also one of the safest ways to handle a toxic agent such as vinyl chloride in that an accidental rupture of the permeation tube will release on the order of 50 g of the gas whereas a cylinder leak may release kg quantities of vinyl chloride. Full details are given in the Appendix.

SECTION VIII

SAMPLING AND ANALYSIS OF AIRBORNE VINYL CHLORIDE

The Environmental Protection Agency is in the process of formulating standards for vinyl chloride monomer (VCM) in ambient air in the vicinity of its processing plants. The Occupational Safety and Health Administration (OSHA) has set standards for the working environment of 1.0 ppm VCM as a time weighted average. Great public concern and debate brought about because of the implication of VCM as a human carcinogen has accelerated the standards setting ahead of the demonstrated capability for its accurate sampling and analysis. Therefore, the performance of the charcoal tube method was critically studied.

A flow dilution system was set up using a vinyl chloride permeation tube (see Section VII), with a dynamic range of 0.5 to 50 ppm VCM. Gaseous samples were drawn from the manifold through charcoal tubes. Gaseous samples were also taken by means of a gas sampling valve on a gas chromatograph both directly from the manifold and downstream from the charcoal tubes. This experimental design provided semi-continuous monitoring and accurate direct calibration with a standard gas source. Commercial tubes (Mine Safety Appliance Company) made for personal monitoring devices and containing 150 mg of charcoal were used throughout the study. All analyses for VCM were performed on a gas chromatograph equipped with a flame ionization detector.

The initial studies were with dry air (less than 10% relative humidity) containing vinyl chloride concentrations of 5, 25 and 50 ppm. Breakthrough volumes were determined at three different sampling rates.

Table 1 represents the results. The 50 ml/min. sampling rate was suboptimal and showed a reduced retention volume. Neither of the 100 ml/min. and 150 ml/min. sampling rates exhibited unequivocally larger retention volumes. However, 100 ml/min. was recommended for reasons of convenience and sampling time. At this rate a sample volume of approximately 10 liters was collected during 100 minutes before 10% breakthrough was reached at 5 ppm VCM.

Recovery of the absorbed VCM from charcoal also was studied. Because the source and treatment history of the charcoal can make a difference in both absorption and desorption, the charcoal used in this study was all from the same batch. It was found that about 87.5% of the VCM that went into the tube could be recovered upon analysis within 2 hours of sampling. Storage of the samples for a period of one week at room temperature decreased the recovery to about 80%. Longer storage time decreased recovery only of low concentration samples; thus after two weeks average recovery was as low as 71% for samples containing 2.5 µg of VCM. Storage time, temperature, sample concentration, and method of tube closure were all important variables affecting recovery.

The charcoal in the commercial tubes was packed in two separate sections, 100 mg in the entrance section, and 50 mg in the rear. These were made for sampling of many compounds, so that if the two sections are analysed separately, absence of significant amounts in the second section demonstrates that breakthrough has not occurred. For VCM, this technique was successful when samples were analysed without delay.

Table 1. RETENTION DATA FOR VINYL CHLORIDE ON CHARCOAL TUBES

Vinyl chloride conc. ppm	Sample rate ml/min.	Mass VCM flow rate µg/min.	Retention* volume liters	Retention* time min.	Total* mass µg
5	50	0.639	10.0	200	127.9
5	100	1.278	9.8	98	125.2
5	150	1.916	29.3	195	373.6
25	50	3.19	7.9	158	504
25	100	6.38	22.8	228	1456
25	150	9.58	20.5	137	1312
50	50	6.38	9.0	180	1285
50	100	12.78	18.1	181	2311
50	150	19.16	14.8	98.7	1891

*At 10% breakthrough from front section of tube.

However, appreciable migration occurred during storage at room temperature, and after 2 weeks recovery of 32 µg was 79% from the front, and 21% from the rear section, which was not far from the 67% - 33% distribution of the weights of charcoal. Migration of VCM can be retarded by storage under refrigeration. However, presence in the second section cannot be regarded as a reliable indication of an invalid sample because of breakthrough.

Studies of the analytical procedure showed a definite relationship between the final recovery and the desorption procedure used. Recovery from tubes stored for two weeks at room temperature depended on whether the two tube sections were combined in one sample vial for desorption with carbon disulfide (90%) or separately desorbed in two vials (total recovery 78%). Thus, if breakthrough was to be checked on each tube it had to be stored under refrigeration and its sections analysed separately, with possibly greater losses. If stored at ambient temperatures, the tube should be analysed as a unit.

The tubes were convenient and inexpensive but required recovery studies for each charcoal batch and particular attention paid to details of analysis. Complete details are given in the Appendix. There is a need for a small device to replace the charcoal tube which has better recovery and is suitable for extended sampling times.

SECTION IX

FOURIER ANALYSIS OF AIR MONITORING DATA

The proliferation of pollutant monitoring activities is now providing massive amounts of data. A major problem has been to obtain the "signal" from the data in the presence of large amounts of "noise" produced by environmental fluctuations. Computers have been utilized to provide information on the statistical distributions of the numbers. Tabulations also have been presented of data averaged by time of day and/or by season. The purpose of this effort was to explore the application of another technique, Fourier analysis of data, which offers the promise of extracting significant new types of information.

Monitoring data shows somewhat irregular fluctuations with time of the concentrations of air pollutants. These can be regarded as the sum of a mean value, and of a series of fluctuations of differing periods, amplitudes, and phases. In the analogous mixture of colors of visible light, resolution into a spectrum can be accomplished by a spectroscope. Recent developments in computer programs make feasible Fourier analysis of air monitoring data to obtain spectra which can serve as equivalent models of the pollutant patterns and aid in understanding atmospheric processes.

Exploratory calculations were carried out on Cincinnati data with a Wang computer and plotter, which was conveniently

available. The results were tabulated and plotted. Some plots are shown in Figures 8 and 9. Surprisingly there is a dip in the amplitudes at a period of seven days, although there are peaks at 3 1/2, 6, and 8 days. Phase information was also tabulated and plotted by the program. The similarity of patterns for pollutants coming from entirely different sources is remarkable. This suggests that atmospheric dispersion processes exert a major role in determining the levels of these pollutants.

More complete analysis appears justified by these exploratory results. A large computer capable of handling hourly data for a year is required, and a program is being prepared for the IBM-370-168. Future work on more data from more cities will clarify the significance of the results. Interesting possibilities for analysing and modelling atmospheric processes are opened up by this technique. Full details are in the Appendix.

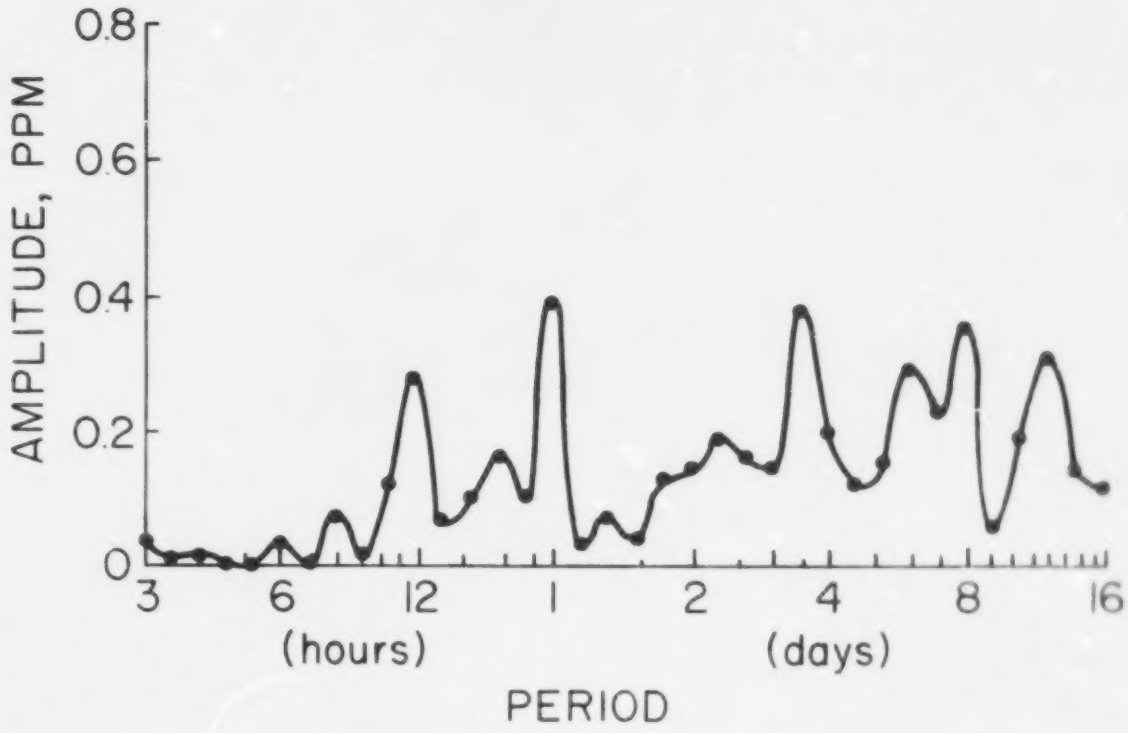

Figure 8. Fourier amplitude spectrum of concentrations of total hydrocarbons in Cincinnati for Oct.-Dec. 1968 (as reported by CAMP).

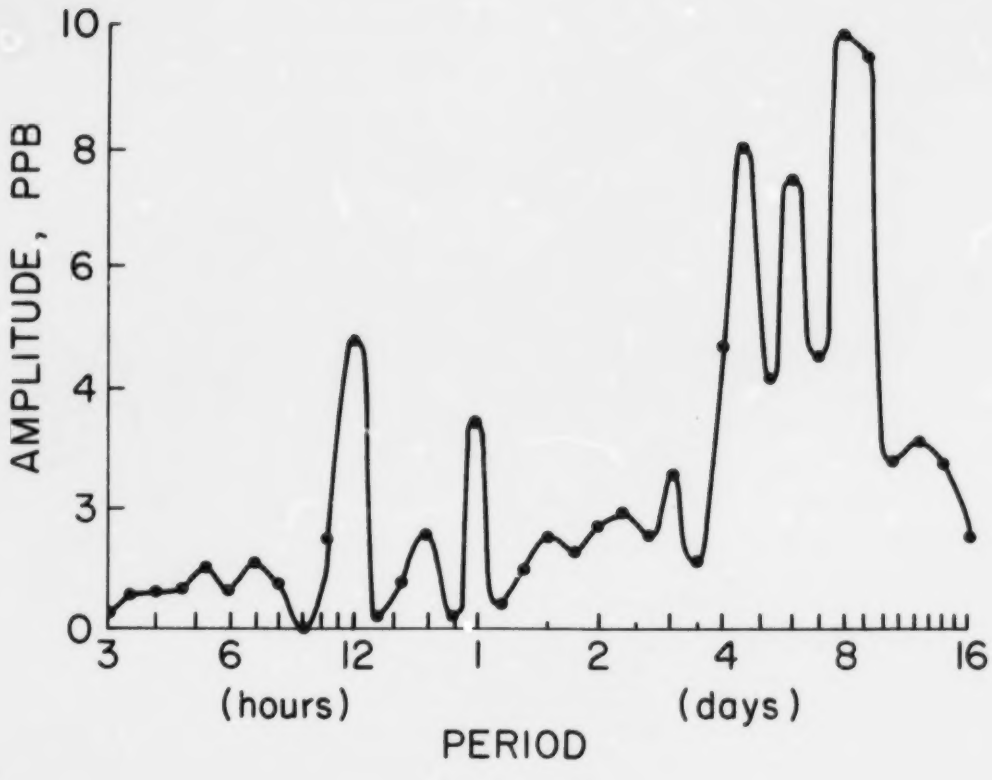

Figure 9. Fourier amplitude spectrum for concentrations of sulfur dioxide in Cincinnati for October, 1968 (as reported by CAMP).

SECTION X

LIST OF PUBLICATIONS AND MANUSCRIPTS*

(Appendices)

A. Cuddeback, J.E., B.E. Saltzman, and W.R. Burg. Solid Absorbent Method for Sampling and Analysis of Nitrogen Dioxide in Ambient Air. J. Air Poll. Control Assoc. (in press) (1975).

B. Saltzman, B.E., W.R. Burg, and J.E. Cuddeback. Continuous Monitoring Instrument for "Reactive" Hydrocarbons in Ambient Air. (submitted to Analytical Chemistry).

C. Birch, S.R., W.R. Burg, and J.E. Cuddeback. Calibration of a Gas Sampling Valve for Gas Chromatography. Anal. Chem. 47, 355 (1975).

D. Burg, W.R., S.R. Birch, J.E. Cuddeback, and B.E. Saltzman. Use of Permeation Tubes for Calibration of Vinyl Chloride Analyses. (to be submitted to Env. Sci. Tech.)

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* Prepared with appropriate acknowledgments to grant for submission to scientific journals. In order not to preclude their acceptance, these are submitted separately as Appendices for confidential use until published.

E. Cuddeback, J.E., W.R. Burg, and S.R. Birch. Sampling and Analysis of Airborne Vinyl Chloride. (submitted to Env. Sci. Tech.).

F. Saltzman, B.E., Fourier Analysis of Air Monitoring Data. In Proceedings of the Symposium on Statistical Aspects of Air Quality Data, p. 11-1 to 11-13. EPA-650/4-74-038, October 1974, Research Triangle Park, N.C.